

Role of Alloying-Atom Size Factor and System Shape Factor in Energetics of bcc Fe under Macroscopic Deformation

Wei Liu,¹ Wei-Lu Wang,¹ Q. F. Fang,¹ C. S. Liu,^{1,*} Qun-Ying Huang,² Yi-Can Wu²

¹Key Laboratory of Materials Physics, Institute of Solid State Physics,
Chinese Academy of Sciences, P. O. Box 1129, Hefei 230031, P. R. China

²Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, P. R. China

(Dated: August 16, 2011)

We present an *ab initio* study of the effect of macroscopic deformation on energetics of twelve alloying elements in bcc Fe under three specially designed strain modes. We find that there exists a universal linear relation of describing the volume dependence of substitutional energy of alloying elements via introducing two factors — the system shape factor (f_{ss}) and the size factor of alloying element M (Ω_{sf}^M): $E_{sub} \sim f_{ss} \Omega_{sf}^M V$. Ω_{sf}^M well describes the effect of intrinsic alloying-atom size and the influence of chemical interaction with matrix atom, and f_{ss} characterizes the degree of system lattice distortion under deformation. This relation is further validated using the published data of stained-modulated doping in GaP [Phys. Rev. Lett. **105**, 195503(2010)].

PACS numbers: 75.50.Bb, 81.05.Bx, 71.15.Mb, 61.82.Bg

Fe-based alloys are among the most widely used materials, of which the ferritic martensitic steels represent a technologically important class of materials with many applications in fission and fusion energy systems. Alloying solutes in Fe-based alloys are of great importance in modifying physical properties, and particularly their contents strongly govern the mechanical performances such as the resistance to hardening and embrittlement under neutron and proton irradiation [1–3]. It is found that the optimal Cr content to improve one special property may be different with that to improve another for bcc Fe based alloys, e.g., the content of 2 to 6% Cr to reduce the irradiation swelling whereas 9% Cr to reduce ductile brittle transition temperature (see Ref. 3 and references therein). Most previous investigations of alloying elements in ferritic martensitic steels have been performed in macroscopically undeformed crystals — free of any macroscopic stain, except those induced by the solutes or defects themselves. Nonetheless, as the structural materials in fission and fusion reactors, the ferritic martensitic steels experience both multiaxial loading and fairly high temperatures, and the internal strain field becomes more complex due to the presence of radiation damages. In fact, all materials usually undergo macroscopic deformations due to externally applied loads or in special in-service conditions. So in recent years many researches have been made on the properties of solutes and point defects under macroscopic deformations based on electronic structure calculations. Gavini found that the volumetric strain associated with a deformation largely governs the formation energies of monovacancies and divacancies in Al and concluded the nucleation of these defects is increasingly favorable under volumetric expansion [4].

Chen *et al.* reported that the strain has remarkable influence on the stability, reorientation and migration of self interstitial atoms (SIA) in bcc Fe [5]: for instance, uniaxial expansion induces a SIA spontaneous reorientation from $\langle 111 \rangle$ to $\langle 100 \rangle$. Zhu *et al.* found in zincblende GaP the impurity formation energy changes monotonically in a linear fashion with the applied external strain and thus proposed that the intriguing unbounded strain-induced change in impurity formation energy can be used effectively to enhance dopant solubility in a wide range of semiconductors [6]. These results raise an interesting question on how macroscopic deformation affects the stability of alloying elements in Fe-based alloys, which to our knowledge remains open. If the macroscopic deformation does influence on the energetics of alloying elements, the aggregation and precipitation may take place consequently, and thus the mechanical performance may be degraded.

In this Letter, we present an *ab initio* study of the effect of macroscopic deformation on substitutional energy of twelve alloying elements (Al, Co, Cr, Cu, Mo, Nb, Ni, Si, Ta, Ti, V, and W [7]) in bcc Fe under three different strain modes. Hydrostatic strain mode is to explore the pure volume change effect, and a set of submodes in both normal strain and shear stain modes are to explore the lattice distortion effect. We find that the macroscopic deformation effect on substitutional energy of alloying elements is governed linearly and universally by two factors, the system shape (lattice distortion) factor and the size factor of alloying element. The size factor of alloying element well describes the effect of intrinsic alloying-atom size and the influence of chemical interaction with matrix atom, and the system shape factor characterizes the degree of lattice distortion under deformation.

The present calculations are performed within spin-polarized density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [8]. The in-

*Author to whom correspondence should be addressed. Email address: csliu@issp.ac.cn

TABLE I: Strain components (%) of each submode in NS and SS.

	e_{11}, e_{22}, e_{33} (NS1-4)/ e_{11}, e_{33}, e_{12} (SS89-85)		
	Vol. contracted by 3.0%	Vol. unchanged	Vol. expanded by 3.0%
NS1	-1.98, -1.0, -0.01	-0.99, 0, 1.0	0, 1.0, 2.01
NS2	-2.94, -1.0, 0.98	-1.96, 0, 2.0	-0.98, 1.0, 3.02
NS3	-3.88, -1.0, 1.97	-2.91, 0, 3.0	-1.94, 1.0, 4.03
NS4	-4.81, -1.0, 2.96	-3.85, 0, 4.0	-2.88, 1.0, 5.04
SS89	-0.996, -1.0, 0.864	0.004, 0, 0.873	1.004, 1.0, 0.881
SS88	-0.985, -1.0, 1.73	0.015, 0, 1.75	1.02, 1.0, 1.76
SS87	-0.966, -1.0, 2.59	0.034, 0, 2.62	1.03, 1.0, 2.65
SS85	-0.906, -1.0, 4.33	0.096, 0, 4.37	1.10, 1.0, 4.41

teraction between ions and electrons is described by the projector augmented wave (PAW) method [9]. Exchange and correlation functions are taken in a form proposed by Perdew and Wang (PW91) [10] within the generalized gradient approximation (GGA). The supercell approach with periodic boundary conditions is used. The supercell contains 127 Fe atoms and one alloying atom. We used an energy cutoff of 350 eV for the plane-wave expansion of the wave functions and a $3 \times 3 \times 3$ k -point mesh for Brillouin zone sampling according to the Monkhorst-Pack scheme. All atomic relaxation calculations are performed at constant volume and shape using the conjugate gradient algorithm. For simplicity the side length of the forementioned bcc cubic supercell in equilibrium is set to be four times of the optimized lattice constant of bcc Fe (2.833 Å). In the calculation of substitutional energy the following formula is used:

$$E_{\text{sub}} = E(n\text{Fe} + 1M) - \frac{n}{n+1} \times E((n+1)\text{Fe}) - E(M), \quad (1)$$

where $E(n\text{Fe} + 1M)$ is the total energy of a bcc cubic supercell containing n Fe atoms and one alloying atom M , $E((n+1)\text{Fe})$ is the total energy of the same bcc cubic supercell filled with only Fe atoms under the same deformation, and $E(M)$ is the energy per atom of pure crystal M in its stablest phase.

In this work, the macroscopic deformation is described by a macroscopic strain tensor with the coordinate axis 1, 2 and 3 being chosen along [100], [010] and [001] directions of the perfect bcc crystal, respectively. Because of strain tensor belonging to a six-dimensional space, a complete characterization of deformation effect on the energetics of alloying atoms is beyond reach. Here we focus on three different modes of strain: hydrostatic strain (HS), normal strain (NS) and shear strain (SS) within relative volume variation from -3.0% to 3.0%. Both NS and SS modes include four submodes: NS1-4 and SS89-85, as listed in Table I. Here, for example, SS89 denotes that the angle between two adjoining surfaces is changed to 89° from initial value 90° . Note that, 1) in NS/SS mode the cube symmetry of the system changes into orthogonality/monoclinism; 2) in each submode of

NS and SS a set of strains are applied in such a way that leads to different volumetric change but the system being kept *similar shape*, in other words, the ratio of three edges and the angle between any two intersected edges of the supercell are unchanged. For example, in submode NS1 the system is in rectangular parallelepiped shape and the ratio of three different edges is fixed at 0.99 : 1.0 : 1.01. From NS4 to NS1 (from SS85 to SS89) the system shape approaches the perfect cube step by step. For all submodes of SS mode the following equations exist: $e_{11} = e_{22}$, $e_{23} = e_{31} = 0$. Of these submodes the strain components with relative volume changes of -3.0%(contracted), 0%(kept at equilibrium) and 3.0%(expanded) are summarized in Table I.

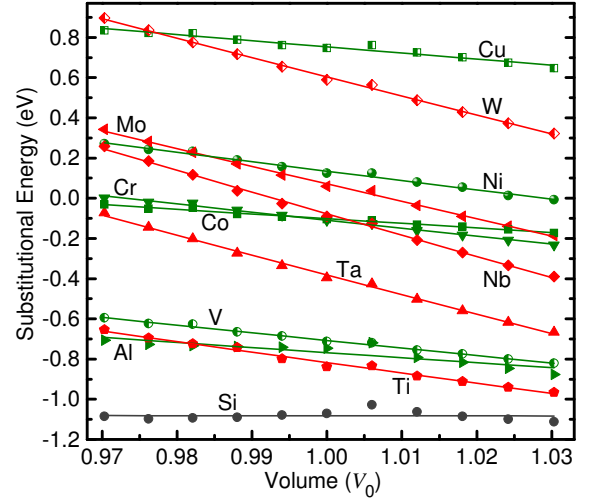


FIG. 1: (Color online) Substitutional energy versus volume for twelve different alloying elements in HS mode. Symbols represent the calculated results and solid lines are the corresponding linear fits.

We first investigate the isotropic volumetric deformation influence on substitutional energy of alloying elements in HS mode. Figure 1 displays the substitutional energy as a function of volume ranging from $0.97V_0$ to $1.03V_0$ in HS mode. In our present work V_0 is the equilibrium volume of the supercell with 128 Fe atom. As can be seen, the substitutional energy of Si is insensitive to isotropic deformation, while with the increase of volume those of Al, Co, Cr, Cu, Ni, and V decrease slowly and those of Mo, Nb, Ta, Ti and W decrease strongly. The results suggest that in HS mode the stability of the alloying elements studied except Si are considerably influenced by hydrostatic volumetric deformation, and these alloying atoms except Si prefer strongly to stay in the expansion zone, which in turn changes the distributions of alloying atoms in bcc Fe, considering the direct correlation between substitutional energy and solubility. For every studied alloying element the substitutional energy depends linearly on the volume with a negative slope (except Si with a much small positive slope), which is

dependent on alloying element. Interestingly, when examining the calculated substitutional energies of each alloying element in each submode of NS/SS with volumes of $0.97V_0$, V_0 , and $1.03V_0$, we find the similar linear volume dependence as in HS mode but with an increased slope. The obtained linearity has been further checked via the added calculations for Al, Cr, and W in NS1, NS4, SS89, and SS85 submodes with volume of $0.982V_0$, $0.994V_0$ and $1.018V_0$, and here only the results of W in NS4 and SS85 submodes are presented in FIG. 2. Figure 2 clearly indicates that, there does exist a similar linear volume dependence of substitutional energy in submodes in NS and SS modes as in HS mode but with a larger slope. For example, in HS the isotropic volumetric increase from $0.97V_0$ to $1.03V_0$ leads to a substitutional energy decrease of 0.234eV for Cr and 0.575eV for W, while in NS4/SS85 the substitutional energy decrease are $0.162/0.116\text{eV}$ for Cr and $0.486/0.442\text{eV}$ for W. Note that $\Delta E_{\text{sub}} (= E_{\text{sub}}|_{V=1.03V_0} - E_{\text{sub}}|_{V=0.97V_0})$ divided by $0.06V_0$ is approximately identical with the element-dependent slope of the forementioned linearity between the substitution energy and volume. These results tell us that in any submode of NS/SS the volumetric deformation effect on the stability of the studied alloying elements except Si is noticeably reduced compared with that in HS mode. Our observed linear volume dependence of substitutional energy are in good agreement with the reported linear behavior of impurity formation energy in semiconductors under hydrostatic strain by Zhu *et al* [6]. They found that the change of impurity formation energy is a linear function of volume and the slope is proportional to the effective size difference between the host and the dopant atom; and trends of the strain-induced change of impurity formation energy for the biaxial and the hydrostatic strain are about the same, except that the effect of the biaxial strain is smaller. Thus, the deformation in NS and SS modes can modulate to some extent the volume dependence of substitution energy compared to pure isotropic volumetric change in HS mode.

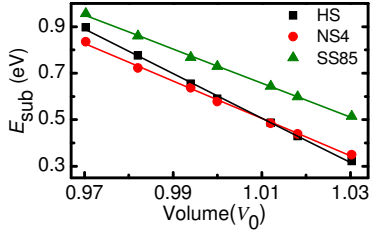


FIG. 2: (Color online) Substitutional energy E_{sub} of W versus volume in HS, NS4 and SS85. Lines are linear fits to the data.

Above results reveal for every studied alloying element the existence of linear volume dependence of the substitutional energy in the same deformation mode (i.e., the system is kept a *similar shape* such as in the HS mode and in the submode of NS/SS mode), but the slope is

dependent on the alloying element. As can be seen from FIG. 1, for the alloying atom with much larger radius the slope is smaller than that with a smaller atomic radius (e.g., Ta and Si). This implies that the difference in atomic size between the alloying atom and the host is a key factor for further exploring the linear volume dependence of the substitutional energy. Recently, Olsson *et al.* proposed a special method to calculate the size factor (Ω_{sf}^M) of single solute atom M in bcc Fe matrix, and found that the calculated Ω_{sf}^M can reflect not only the effect of the solute atom size but also the influence of the chemical interaction with the matrix [11]. Following this method, we first obtain the bulk modulus B for every binary alloy by fitting the linear relation between pressure and volume ($\Delta P = -B\Delta V/V_0$) in HS mode with volume varying from $0.97V_0$ to $1.03V_0$. Then the size factor of the alloying atom is calculated by

$$\Omega_{\text{sf}}^M = -V_0\Delta P_{\text{ex}}/(\Omega_{\text{Fe}}B), \quad (2)$$

where ΔP_{ex} is the excess pressure of the binary alloy and Ω_{Fe} is the atomic volume of bcc Fe. ΔP_{ex} is calculated by subtracting the external pressure of pure bcc Fe matrix in HS from that of the binary alloy in HS with the same equilibrium volume V_0 . If the Ω_{sf}^M of alloying atom correctly describe the intrinsic size difference and the change in atomic interaction, then there may exists a general (or universal) law of the macroscopic deformation effect on substitution energy. So we replot the substitution energy changes ΔE_{sub} of twelve alloying elements as a function of Ω_{sf}^M in FIG. 3. To our surprise, as displayed in FIG. 3 it is found that in those modes/submodes whose system being kept a similar shape ΔE_{sub} exhibits a universal dependence on the Ω_{sf}^M : for all studied alloying elements ΔE_{sub} (i.e. the slope of linear volume dependence of E_{sub}) is approximately inverse proportional to Ω_{sf}^M . In Ref. 6, it is obtained as a first order approximation that $E_{\text{dop}} \sim \alpha(V_{\text{host}} - V_{\text{host+dopant}})V$, where α is the elastic constant, $V_{\text{host+dopant}}$ is the equilibrium volume of the system with the dopant and V_{host} is the equilibrium volume of the host lattice. This formula can also well describe the linear relation of substitutional energy versus volume in FIG. 1, and the slope is determined by $\alpha(V_{\text{host}} - V_{\text{host+M}})$. Based on the above discussion $\alpha(V_{\text{host}} - V_{\text{host+dopant}})$ in Ref. 6 corresponds to Ω_{sf}^M in present work. Therefore, using Eq. 2 (where ΔP_{ex} is replaced by $-B\Delta V_{\text{ex}}/V_0$ and Ω_{Fe} is replaced by Ω_{Ga}) and the data summarized in Table I in Ref. 6 on strain-enhanced doping in semiconductors, we calculate Ω_{sf}^D of doping elements in GaP. The doping energy difference ΔE_{dop} resulted from the strain change between -2% and 2% in HS mode as reported in FIG. 1 in Ref. 6 is redisplayed as a function of the calculated Ω_{sf}^D in the inset of FIG. 3. This inset figure clearly indicates that for doping of zincblende GaP the doping energy changes resulted from hydrostatic strain show a similar universal dependence on the Ω_{sf}^D , though the doping energies of these elements ex-

TABLE II: The system shape factor of each NS/SS submode in unit of $\text{eV}\text{\AA}^{-3}$. The system shape factor in HS mode is $-2.51 \text{ eV}\text{\AA}^{-3}$.

Mode	NS4	NS3	NS2	NS1	SS85	SS87	SS88	SS89
f_{ss}	-2.31	-2.38	-2.40	-2.48	-2.39	-2.40	-2.45	-2.48

hibit different, even opposite volume dependence. Thus the $\Omega_{sf}^{M/D}$ is a suitable factor which well describes the intrinsic size difference and the change in atomic interaction between alloying/doping atom with host atom and produces a universal effect of pure volumetric deformation. In addition, as forementioned and shown in FIG. 2 the element-dependent slope of the linearity between the substitution energy and volume is larger in any submode of NS/SS than in HS mode, suggesting that the system shape factor (f_{ss}) should be introduced to describe the lattice distortion of system under strained conditions. So the substitutional energy change due to macroscopic deformation can be described universally by the following formula:

$$E_{\text{sub}} = f_{ss}\Omega_{sf}^M V + I. \quad (3)$$

Here, the constant/intercept I is dependent on both the alloying element and the strain submode. By linear fitting of the calculated ΔE_{sub} versus Ω_{sf}^M the f_{ss} of each NS and SS submode is obtained and listed in Table II. As can be seen, from NS4 to NS1 and from SS85 to SS89 the system lattice distortion is weakened, the system shape factor values become smaller and approaches the value in HS mode where no lattice distortion. This result suggests that the system shape factor can well describe the system lattice distortion. Therefore, the macroscopic deformation effect on substitutional energy can be divided into two parts: the system shape distortion effect described by the f_{ss} factor and the pure volumetric change effect generalized by the Ω_{sf}^M for different alloying elements. In shape/lattice distorted systems the pure volumetric change effects on substitutional energy is enlarged for the alloying element who has negative size factor, and is reduced for the one who has positive size factor compared with the cases in perfect cubic systems.

In summary, the *ab initio* calculations reveal that within volume change ranging from $0.97V_0$ to $1.03V_0$ the macroscopic deformation effect on the substitutional energy of alloying elements can be divided into pure volume change effect and lattice distortion effect and be well described by a universal and simple relation: $E_{\text{sub}} \sim f_{ss}\Omega_{sf}^M V$. This relation should be beneficial to understanding the mechanical performance degrading of Fe-based alloys under deformation. We believe that this relation can be generalized to other systems in studying substitutional or doping energy change under deformed condition. In addition, in the lattice distorted systems the pure volume change effects on substitutional energy

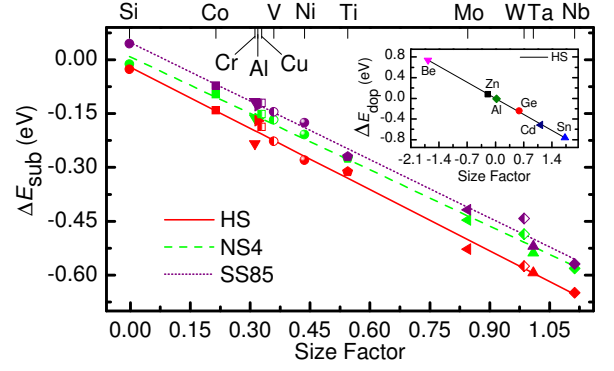


FIG. 3: (Color online) Substitutional energy change ΔE_{sub} versus size factor in HS, NS4 and SS85 with volume change from $0.97V_0$ to $1.03V_0$ for twelve alloying elements. Inset: The doping energy difference resulted from the strain changes between -2% and 2% in HS mode in GaP versus size factor of dopant. Lines are linear fits to the data.

is enhanced for those alloying elements who have negative size factor, and is reduced for those who have positive size factor compared to the cases without lattice distortion, which may be instructive to design better materials.

This work was supported by the Innovation Program of Chinese Academy of Sciences (Grant Nos.: KJXC2-YW-N35 and XDA03010303) and the National Magnetic Confinement Fusion Program (Grant No.: 2009GB106005), and by the Center for Computation Science, Hefei Institutes of Physical Sciences.

- [1] W. C. Leslie, Metall. Trans. **3**, 5 (1972).
- [2] H. Ishii, T. Kawarazaki, Y. Fujimura, Metall. Trans. A **15A**, 679 (1984).
- [3] P. Olsson, C. Domain, and J. Wallenius, Phys. Rev. B **75**, 014110 (2007).
- [4] V. Gavini, Phys. Rev. Lett. **101**, 205503 (2008).
- [5] Z. Chen, N. Kioussis, N. Ghoniem, and D. Seif, Phys. Rev. B **81**, 094102 (2010).
- [6] J. Zhu, F. Liu, G. B. Stringfellow, S.-H. Wei, Phys. Rev. Lett. **105**, 195503 (2010).
- [7] In hydrostatic strain we calculated the substitutional energies of Mn: the value is almost constant (0.118 ± 0.032 eV) in the volume range from $0.970V_0$ to $1.024V_0$, but it changes to -0.048 eV at $1.03V_0$. We do not know the whys of this unusual result of Mn. So the result of Mn is not presented in this paper.
- [8] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558(R)(1993); G. Kresse and J. Furthmüller, *ibid.* **54**, 11169 (1996).
- [9] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999); P. E. Blöchl, *ibid.* **50**, 17953 (1994).
- [10] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- [11] P. Olsson, T. P. C. Klaver, and C. Domain, Phys. Rev. B **81**, 054102 (2010).